HANDBOOK OF PLASMA IMMERSION ION IMPLANTATION AND DEPOSITION

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Edited by

André Anders

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CONTENTS

Contributors	χV
Preface	xix
1 Introduction John R. Conrad	1
 1.1 Concept of Plasma Immersion Ion Implantation / 2 1.2 Comparison of Traditional Ion Beam Implantation with Plasma Immersion Ion Implantation / 3 1.3 Combining Plasma Immersion Ion Implantation with Deposition / 6 	
 1.4 Development of the Basic Science of Ion Implantation / 7 1.5 Development of Conventional Beamline Ion Implantation / 9 	
1.6 History of the Development of Plasma Immersion Ion Implantation / 11	
1.7 Commercial Applications of PIII&D / 201.8 Speculation on Future Developments in PIII / 22	
PART I FUNDAMENTALS 2 Fundamentals of Plasmas and Sheaths Michael A. Lieberman	29
 2.1 Plasmas / 38 2.1.1 Basic Plasma Equations and Equilibrium / 38 2.1.2 Collisions / 52 2.1.3 Plasma Dynamics / 64 2.1.4 Diffusion and Transport / 77 2.1.5 Discharge Equilibrium / 92 	

vi	CONTENTS	
2.2	Sheaths / 104 2.2.1 Basic Concepts and Equations / 104 2.2.2 Bohm Sheath Criterion / 107 2.2.3 High-Voltage Sheaths / 115	
	Ion Implantation and Thin-Film Deposition Michael Nastasi, Wolfhard Möller, and Wolfgang Ensinger	125
3.1	Ion-Solid Interaction / 125 3.1.1 Introduction / 125 3.1.2 Basic Principles / 126 3.1.3 Ion Stopping / 140 3.1.4 Ion Range Calculations / 145 3.1.5 Radiation Damage / 149 3.1.6 Thermal Spikes / 150 3.1.7 Radiation-Enhanced Diffusion / 151 3.1.8 Sputtering / 155 3.1.9 Distribution of Implanted Atoms / 159 3.1.10 Ion-Solid Simulations / 161 3.1.11 Ion Mixing / 167 Ion-Assisted Thin-Film Growth / 173	
J.2	3.2.1 Introduction / 173 3.2.2 Film Stoichiometry / 177 3.2.3 Film Growth and Structure / 181 3.2.4 Film Properties / 209	
	Fundamentals of Plasma Immersion Ion Implantation and Deposition Blake P. Wood, Donald J. Rej, André Anders, Ian G. Brown, Richard J. Faehl, Shamim M. Malik, and Carter P. Munson	243
4.1 4.2	Introduction / 243 Transient Sheaths / 246 4.2.1 Introduction to Transient Sheaths / 246 4.2.2 Collisionless Sheath Model / 247 4.2.3 Extensions to the Collisionless Sheath Model / 249	
4.3 4.4 4.5 4.6	Secondary Electron Emission / 263 Implantation in Pipes and Holes / 268 Implant Uniformity and Retained Dose / 271 Implantation of Nonconducting Materials / 275	

4.7 4.8	Implantation at Elevated Temperatures / 277 Plasma Immersion Ion Implantation with Deposition / 281 4.8.1 Introduction / 281 4.8.2 Plasma Immersion Ion Implantation and Deposition with Cathodic Arc Plasmas / 282 4.8.3 Sacrificial Layers / 288 4.8.4 Ion Mixing and Layer Adhesion / 291 4.8.5 PIIID with Multielement Metal Plasmas / 292 4.8.6 PIIID in the Presence of Reactive Gases / 292	
4.9	Electrical System Requirements / 293	
	laterials Characterization and Testing lethods—A Brief Survey Evin C. Walter, Kumar Sridharan, and Michael Nastasi	303
5.1 5.2	Introduction / 303 Materials Characterization of Surfaces Treated by Plasma Immersion Ion Implantation / 304 5.2.1 Retained Ion Dose, Implanted Ion Distribution, and Composition of the Implanted Region / 304 5.2.2 Precipitates or Secondary Phase Formation / 315 5.2.3 Surface Roughness / 319	
5.3	Materials Characterization of Coatings Synthesized by Plasma Immersion Ion Implantation and Deposition / 320 5.3.1 Composition / 320 5.3.2 Crystallinity / 321 5.3.3 Morphology / 321 5.3.4 Thickness and Index of Refraction: Ellipsometry / 321	
5.4	Materials Testing of Surfaces Treated by Plasma Immersion Ion Implantation / 322 5.4.1 Hardness and Elastic Modulus / 322 5.4.2 Tribological Testing / 324 5.4.3 Corrosion Testing / 328	
5.5	Materials Testing of Coatings Synthesized by Plasma Immersion Ion Implantation and Deposition / 332 5.5.1 Adhesion / 332 5.5.2 Stress / 334 5.5.3 Resistivity / 334	

PART II TECHNOLOGY

6	Design	of a PIII&D Processing Chamber	343	
		atossian, George A. Collins, Paul K. Chu,		
		P. Munson, and Joseph V. Mantese		
6.1 6.2 6.3	Backg Gener	Introduction / 343 Background / 344 General Trends for Chamber Size, Voltage, and Processing Power / 345		
<u> </u>		n Guidelines and Scaling Relationships II&D Chambers / 350		
	6.4.2	Chamber Size / 350 Chamber Structure / 353 Chamber Material / 356		
6.5	Vacuu	um Pumps / 356		
	6.5.2 6.5.3	Pumping Stages / 356 Relation of Pumping Speed, Outgassing, and Pressure / 357 Determination of the High-Vacuum Pumping Speed / 358 Determination of High-Vacuum Gas Throughput / 360 Types of High-Vacuum Pumps / 361		
6.6 Fixtures / 364		res / 364		
		Fixture Types / 364 Design, Electrical Insulation, and Weight Capacity of Fixtures / 364		
6.7	6.7.1 6.7.2 6.7.3	Heating and Cooling of Chamber Walls / 367 Heating and Cooling of Chamber Walls / 367 PIH&D with Chamber Walls at Elevated Temperature / 369 Coating Protection by Internal Shields / 371 X-ray Shielding / 372)	
6.8	Proces	ss Diagnostics and Control / 374		
		In Situ Diagnostics / 374 Process Control of a PIII&D Facility / 375		
7	André A	a Sources nders, Jacques Pelletier, Dan M. Goebel, Blake P. Wood, Brown, Wolfgang Ensinger, and Michel Tuszewski	381	
7.1 7.2		Thermionic Discharge Cathodes / 386	ļ	

7.3	7.3.1 7.3.2	Unassisted Discharge / 393 Assisted Discharge / 396
7.4	7.4.1 7.4.2 7.4.3 7.4.4	Introduction / 398 Introduction / 398 Capacitive Source Configuration / 398 Plasma Parameters / 400 DC Self-Bias / 401 Electron Heating Mechanisms / 403
7.5	7.5.1 7.5.2 7.5.3 7.5.4	tively Coupled RF Plasma Sources / 403 Introduction / 403 Inductively Coupled Plasma Configurations / 403 Induction Coupling / 404 Plasma Parameters / 406 Pulsed Operation / 408
7.6	7.6.1 7.6.2 7.6.3 7.6.4	Specificity and Classification of Microwave Plasma Sources / 409 Microwave Circuit of a Plasma System / 411 Design and Characteristics of Microwave Plasma Sources / 412 Scale-Up of Microwave Plasma Sources / 423 Perspectives for Microwave Discharges and Multipole Plasmas in PIII&D / 428
7.7	7.7.1 7.7.2 7.7.3	te Gas Plasma Sources / 430 Introduction / 430 Streaming Plasma from a Filament Source / 430 End-Hall Plasma Source / 430 Constricted Plasma Source / 432
7.8	7.8.1 7.8.2	Long-Pulse and DC Cathodic Arc Plasma Sources / 437
7.9	7.9.1 7.9.2 7.9.3	Sources of Plasma and Vapor / 444 Spotless Cathodic Arcs / 444 Anodic Vacuum Arcs / 444 Laser Plasma Source / 446 Sputtering / 446 Thermal and Electron Beam Evaporation / 451

8 Pulser Technology

	Dan M. Goebe and William A	el, Richard J. Adler, Dexter F. Beals, . Reass	
8.1	8.1.1 Intro 8.1.2 Pulse	esign Considerations for PIII&D Pulsers / 467 oduction / 467 er Impedance / 470 er Circuits / 472	
8.2	8.2.1 Intro 8.2.2 Hard	Pulsers / 477 oduction: Advantages of Hard-Tubes Pulsers / 477 d-Vacuum-Tube Types / 477 d-Tube Modulator Circuits / 479	
8.3	8.3.1 Intro 8.3.2 Com	ed on Thyratrons with Pulse-Forming Networks / 485 oduction: Advantages of Thyratron Switches / 485 abining Thyratrons and Pulse-Forming Networks / 486 racteristics of Pulse-Forming Networks / 487	
8.4	8.4.1 Intr 8.4.2 Circ 8.4.3 Insr 8.4.4 Thy 8.4.5 Gat 8.4.6 Me Fiel 8.4.7 Bip 8.4.8 Pov Soli 8.4.9 Pro	Modulators / 492 roduction: Advantages of Solid-State Modulators / 492 cuits for High-Power Solid-State Pulsers / 493 ulated-Gate Bipolar Transistors / 494 yristors (SCR) / 494 te Turn-Off Devices / 495 tal-Oxide-Semiconductor ld Effect Transistors / 496 over Considerations and Limitations of id-State Devices / 496 otection and Implementation of Solid-State Devices / 498 vice Drive Circuits / 500	3
8.5	8.5.1 Intro 8.5.2 Tran 8.5.3 Exar 8.5.4 Gene 8.5.5 Harc 8.5.6 High	sformer Design for PIII&D / 501 oduction: Use of Pulse Transformers / 501 asformer Design / 502 mple of Empire Hard Chrome Pulser / 506 eral-Purpose IGBT/Transformer Pulser / 506 d-Tube/Transformer Pulser / 509 n-Voltage/Transformer Pulser / 509	51 5
9		Safety Issues Related to PIII&D ls, André Anders, and Jesse Matossian	515
9.1 9.2	Introduction Electrical S	•	

467

	9.2.2 9.2.3 9.2.4 9.2.5 9.2.6	Inductively Stored Energy / 518 Safety Precautions Related to Stored Energy / 519 Lockout and Tagout Procedures / 519	
9.3	9.3.1 9.3.2	Some Definitions and Relevant Considerations / 524 Nonionizing Radiation / 525 Ionizing Radiation / 531	
9.4	9.4.1	m and Chamber Safety / 539 Implosion Hazards / 539 Chamber Entry and Confined Space Hazards / 540 Compressed Gas Containers / 541	
9.5	9.5.1 9.5.2 9.5.3	,	42
PAF	RT III	APPLICATIONS	
10	Kumar Kevin C	emiconductor Applications of PIII&D Sridharan, Simone Anders, Michael Nastasi, C. Walter, André Anders, Othon R. Monteiro, Olfgang Ensinger	553
10.1	10.1. 10.1. 10.1.	1 Introduction / 553 2 Improvements of Wear Resistance / 555 3 Improvements of Corrosion Resistance / 559 4 Results of Industrial Field Tests / 566	
10.2	Diam 10.2.2 10.2.2 10.2.4 10.2.4	Preparation of DLC by PIIID / 570 Enhancement of Adhesion of DLC Coatings / 571 Microstructure and Characterization of DLC Coatings /	571

XII	CONTENT	-0
AII	CONTEIN	0

10.3	10.3.1 10.3.2	Synthesis of a-C Films / 578 Deposition and Properties of a-C Films Synthesized by Cathodic Arc Carbon Plasmas / 579 Amorphous Hard Carbon for Tribological Applications in the Magnetic Storage Industry / 587	
10.4	10.4.1 10.4.2 10.4.3	Plasma Immersion Ion Implantation in Combination with Thin-Film Deposition / 595 Postdeposition PIII Treatment of Coatings / 596 Deposition and PIII Treatment as In-Line Process / 600 Triode Sputter Deposition / 606 Metal Plasma Immersion Ion Implantation and Deposition / 609	
10.5	10.5.1 10.5.2 10.5.3	Introduction / 614 Nickel Alkaline–Electrolyte Cells / 615 Lithium Cells / 616 Lead Acid Cells / 619	
10.6	10.6.1 10.6.2	Introduction / 621 Modification of the Wettability of Polystyrene Surfaces / 622 Protection of Polymers from Severe Oxidizing Environments / 622 Improvement of Polymer Wear Resistance by Mesh-Assisted PIII / 623	
		nductor Applications hu, Nathan W. Cheung, Chung Chan, Bunji Mizuno, and Monteiro	637
11.1 11.2		Station / 637 Junction Formation / 639 Shallow Junctions Formed by PIII / 639 Plasma Immersion Ion Implantation of BF ₃ /SiF ₄ / 641 Doping Using Hydrides / 647 Contamination Studies / 648	
11.3		nel Displays / 651 on-Insulator Fabrication / 652 Introduction to SOI Fabrication Processes / 653	

11.4.	2 SPIMOX (Separation by Plasma Implantation of Oxygen) / 653	
11.4. 11.4.	•••	
11.5.	ocavity Engineering / 663 Gettering Effects / 663 Buried Light-Emitting Porous Silicon / 665	
11.7 Meta	ch Doping / 667 Ilization Technology for Deep Trench Filling / 669 Iusions / 673	
Appendix	A Survey of PIII&D Intellectual Property Jesse Matossian	683
A.2 Sumr	duction / 683 hary / 684 led Listing of the Worldwide Issued Patents / 685	
Appendix	B Constants and Formula	705
Appendix	C Frequently Used Acronyms	711
Appendix	D About the Authors	715
Index		727

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PREFACE

Plasma processing of materials has matured in recent decades at an incredible speed. Conventional techniques have been upscaled, in situ monitoring and computer-aided feedback controls have become standard, and new processing methods have been invented. The turn of the millennium is a welcome occasion to step back for a moment from the fast pace of day-to-day operation of research, development, and high-tech production. Before we "immerse" ourselves into technology details, let's step back and have a look at the big picture. Materials research and development is a cornerstone of modern industry; it provides enabling technologies for the information age. There would be no high-speed computing, wide bandwidth network connections, wireless communication, and the like without modern materials technologies. Innovative process solutions and materials are also developed for the more traditional areas in manufacturing and transportation, including the space and automotive industry. At the same time, scientists, engineers, and economists are today more aware than ever of the environmental impact of modern technologies. In fact, the need to replace technologies that have severe negative environmental impact has become a major driving force for the development of better alternatives.

One of the emerging technologies is plasma immersion ion implantation (PIII), also known as plasma source ion implantation (PSII) or plasma-based ion implantation (PBII). In order to appreciate PIII, we will start with a quick comparison with conventional beamline ion implantation. Energetic ion beams are obtained from ion beam sources by extracting ions from a plasma and accelerating them using the electric field across a single or multiple aperture grid system. The electric potential difference between the grids is high: often tens or hundreds of kilovolts, and sometimes the ion energy is further increased to the mega-electron-volt range utilizing accelerator stages. The ion beam cross section is usually small (compared to the substrate area), with three important consequences: (1) feasibility of magnetic ion charge and mass separation, (2) the need for scanning the beam across the surface area to obtain large implantation areas with sufficient dose uniformity, and (3) low dose rates and long processing times. PIII, in contrast, is a very different approach that leads to opposite features. The substrate to be implanted is immersed in the processing plasma, and negative high-voltage pulses are applied so as to form a

conformal electric sheath (space charge layer) between the substrate and the plasma. Ions located in or entering the sheath from the plasma side are accelerated by the sheath's electric field. They are implanted into the substrate when they impact the substrate. The fascinating idea of this approach is to eliminate the need for ion beam extraction, focusing, transport, scanning, and other manipulation. These are some of the advantages of PIII. Other features, including drawbacks and limitations, will be discussed in detail in this handbook.

Plasma calculations by Melvin Widner at Oak Ridge National Laboratory in the 1960s and the pioneering work of Richard Adler at Mission Research Corporation in the early 1980s prepared the field. However, it was the work of John Conrad and co-workers at the University of Wisconsin at Madison that was pivotal for the birth and recognition of the PIII concept. They reported on the first plasma immersion ion implantation results with nitrogen plasmas in 1986. Nitrogen plasmas were dominant in the early years because one could form subsurface nitrides at relatively low temperatures with excellent mechanical and chemical properties. In the following years, the physical basis has been developed by a number of groups, and new applications have been explored. I'm grateful that John agreed to write the first chapter of this handbook, describing the early development of PIII and its relation to other techniques, in particular to ion nitriding. He puts the development of PIII&D in a historical perspective by comparing it with traditional beamline ion implantation. He outlines the physics and original applications of PIII.

The early PIII work used gaseous plasmas such as nitrogen plasmas. By extending PIII to condensable (metal or organometallic) plasmas and vapors, the field was expanded from pure ion implantation to thin-film deposition. As a consequence, the letter *D* for deposition was included in the acronym, now PIII&D. The title of this handbook, plasma immersion ion implantation *and deposition*, reflects this development.

If condensable plasma species such as metal ions are involved, this concept translates into ion implantation and ion deposition phases. Pulsing the substrate implies high-energy phases (bias pulse on, ion implantation) and low-energy phases (bias pulse off, ion deposition). Figure 1 illustrates the hybrid character of PIII&D. In general, PIII&D equipment and processes may be operated in a pure plasma immersion ion implantation (PIII) mode or a pure plasma immersion ion deposition (PIID) mode (the latter has existed before PIII was invented, as pointed out in Chapter 1). The following acronyms are used in this book: PIII for plasma immersion ion implantation with gaseous plasmas, PIIID for plasma immersion ion implantation and deposition with condensable, film-forming plasmas and vapors, and PIII&D when generically referring to both.

Today, at the turn of the millennium, PIII&D in its various forms has become a mature technology with first applications of industrial size. Our knowledge has been compiled and described in several book chapters, and about 1000 articles have been published in a variety of scientific journals.

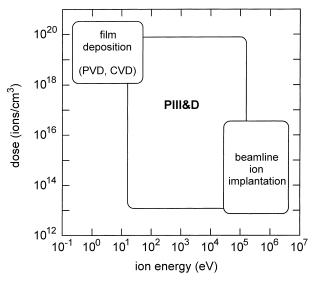


Figure 1 Relation of PIII&D to ion implantation and thin-film deposition.

Several International Workshops on Plasma-Based Ion Implantation have demonstrated the vitality of the field. The time has come to consolidate the work in a single monograph dedicated to this field; this handbook describes the PIII&D work from its beginnings to the end of the twentieth century.

Plasma physicists, materials scientists, chemists, pulse-power engineers, and many others have contributed to the development of PIII&D, a field at the interface of several scientific disciplines. It seemed mandatory to include a rather large number of authors and draw from their different and complementary experience and expertise.

This book is composed of three parts: Fundamentals, Technology, and Applications. In Part I, the basics of plasmas and plasma sheaths are introduced by Michael Lieberman. Background information on ion implantation and thin-film formation is provided in Chapter 3, coordinated by Michael Nastasi. In Chapter 4, the fundamental processes of PIII and their extension to PIIID are introduced by Blake Wood and co-authors. This chapter is the core of the handbook; it is not coincidental that its title is practically identical with the title of the Handbook. If you are familiar with the basics of plasmas, sheaths, ion implantation and thin-film deposition, and you would like to learn about PIII&D, I would recommend that you go straight to Chapter 4. Chapter 5, coordinated by Kevin Walter, gives an overview of materials analysis and testing techniques. This chapter will be found useful by those who want to be reminded of the various methods for determining the qualitative and quantitative effects of PIII&D treatment. Of course, all of the chapters contain numerous references that allow the reader to probe deeper in the original literature. Chapter 5 concludes the fundamentals part of this handbook.

In Part II, Jesse Matossian and co-authors discuss design issues of PIII&D processing chambers, process control, part handling, and other information relevant to the practical design and use of PIII&D vacuum equipment. In Chapter 7, coordinated by myself, plasma sources and the technical means of plasma production and control are discussed. Chapter 8, coordinated by Dan Goebel, deals with the pulser technology necessary to achieve suitable substrate bias pulses. The *Technology* part is concluded by Chapter 9, coordinated by Dexter Beals, in which safety and health issues are discussed that are related to the variety of PIII&D processes.

Part III starts with nonsemiconductor applications such as the reduction of wear and corrosion of PIII-treated workpieces, the core application of PIII in its early years. Chapter 10, coordinated by Kumar Sridharan, also includes applications of PIIID such as the deposition of compound layers and finetuned hard amorphous (diamondlike) carbon films. Finally, Chapter 11, coordinated by Paul Chu, describes modern applications in semiconductor research and industry such as the PIII formation of ultrashallow junctions.

Twenty-nine distinguished authors from six countries have contributed to this book. I feel privileged that I had the opportunity to work with them and that I was given the honor of coordinating and editing this handbook. The authors are portrayed in short biographies compiled in Appendix D.

Many individuals, governmental research organizations, and private corporations supported PIII&D research and publications, including, but not limited to, the U.S. Department of Energy, Department of Defense, Department of Commerce, the National Science Foundation, the State of Wisconsin, General Motors, Sematech, North Star Research Corporation, Diversified Technologies Inc., Poole Ventura, Empire Hard Chrome, and Hughes Research Laboratories. Development of PI³ in Australia has been supported by the Australian Nuclear Science and Technology Organisation, and the Industry Research and Development Board of Australia. PIII-related R&D in Germany has been supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (Federal Ministry for Education, Science, Research, and Technology, BMBF) and by the Deutsche Forschungsgemeinschaft (German Research Community, DFG). Support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Sciences, is gratefully acknowledged by Mike Nastasi for the writing of Section 3.1. I personally would like to thank Ian Brown, Group Leader at Lawrence Berkeley Laboratory and co-author of Chapters 4 and 7, for his scientific and linguistic help over the past years. Dave Busby was of great help in "computer emergencies." Keith Gershon, Electrical Safety Engineer at Lawrence Livermore National Laboratory, is acknowledged for critical reading of Chapter 9. The authors of Chapter 11 would like to thank Dixon Tat-kun Kwok for his help in preparing some of the Chapter 11 figures. Bunji Mizuno, co-author of Chapter 11, expresses his gratitude to Horiyuki Mizuno, former executive vice president of Matushita Electric Industrial Co., his colleagues Ichiro Nakayama and Michihiko Takase, and the support by the Science and

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André Anders

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